UDC 666.642.3.004.18

GLAZED MAJOLICA ARTICLES PRODUCED BY SINGLE-STAGE FIRING

I. A. Levitskii[1] and V. A. Biryuk[1]

Translated from Steklo i Keramika, No. 12, pp. 27 – 30, December, 2000.

Results of synthesis of ceramic mixtures for producing glazed majolica articles employing single-stage firing technology are presented. The features of gas formation and formation of the structure of the crock and a clear glaze layer are studied. Criteria for selection of the mixture composition and the time/temperature parameters of the heat treatment are determined.

Production of household and applied-art majolica articles is a promising field in Belarus, due to the available production facilities, the local polymineral material, and the stable demand. In recent years, there has been a trend in world practice to use single-stage firing for production of majolica articles based on argillaceous materials of various mineralogical compositions [1, 2]. This technology is especially topical, since it makes it possible to reduce the consumption of energy and raw materials (imported clays, fluxes, and grog additives).

With the aim of developing mixture compositions for majolica products of single-stage firing based on low-melting clays and studying the possibility of controlling the phase composition and properties of the ceramic materials, the authors used a combination of several polymineral clays of different mineralogical compositions and addition of local kaolinite materials to the ceramic mixtures. This method fosters expansion of the sintered-state interval, improvement of a number of physicochemical properties and, possibly, some stabilization of the chemical composition of the ceramic mixtures. At the same time, the effect of a complex flux that, in addition to alkali oxides, contained alkali-earth metal oxides was investigated.

In the course of preliminary studies, certain features of local argillaceous materials were identified. For instance, low-melting clays of Belarus are not sinterable and have virtually no sintered-state interval. They are characterized by a polymineral composition, a substantial content of free quartz (up to 35 – 38%) and colorant oxides (a content of $Fe_2O_3 + TiO_2$ equal to 5 – 8%), and the presence of carbonate inclusions (up to 7%).

The specific features inherent in local polymineral clays determine their specific behavior in firing and the distinctive structure and properties of ceramics based on this material. Thus, the substantial quantity of carbonates fosters formation of calcium and magnesium silicates and aluminosilicates in firing (in our case, anorthite), which results in decreased shrinkage of the material. The increased content of Fe_2O_3 in the clay together with the substantial content of alkali metals fosters intense dissolution of free quartz in the melt.

The experimental ceramic mixtures selected for the investigation contained kaolinite-hydromica clay from Lukoml' deposit (Vitebsk Region) and kaolinite-hydromica-montmorillonite clay from Gaidukovka deposit (Minsk Region) [3]. Container glass cullet was introduced as the alkali-bearing component, and nepheline-sienite as the component containing alkali-earth oxides. Experimental mixtures with a complex-flux additive were used to mold samples that were subjected to various heat-treatment procedures.

Thermal analysis of the ceramic mixtures indicated that processes of decomposition and phase formation that are regular for mixtures based on polymineral clays occur in these mixtures in heating. They include a low-temperature effect that correlates with removal of molecular water and subsequent effects that correlated with removal of constitutional and hydroxyl water, partial amorphization of the material, destruction of the kaolinite structure, dehydration of hydromica, and decarbonization reactions.

The considered fluxing additives introduced into the mixtures do not have a perceptible effect on the shift of the thermal processes toward a temperature decrease. At the same time, it was found that the maximum gas emission in most ceramic mixtures is observed at a temperature of 850°C, and in some compositions it occurs at lower temperatures (820 – 850°C). The weight loss here is 3.5 – 4.8%. Based on the thermal analysis, it was found that an expedient heat-treatment procedure is a process with an isothermal hold at 850 – 900°C for 20 – 25 min for more complete decomposition of the carbonate components.

[1] Belarus State Technological University, Minsk, Belarus.

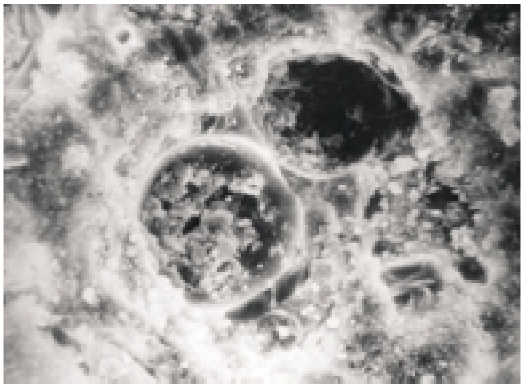

Fig. 1. Electron microscope photograph of the structure of ceramic samples fired at a temperature of 975°C.

It is known that a change in the physicochemical properties of ceramic materials is determined not only by the chemical and mineralogical composition but also by the features of the formed structure of the product of the firing. That is why we also performed a study of the structure of the samples using x-ray phase analysis and electron microscopy.

The results of the study indicated that the main crystal phases are α-quartz, anorthite, and hematite, and the highest peaks belong to α-quartz, which is quite regular, since local clays usually contain substantial quantities of free quartz. In changing the experimental-mixture compositions, it can be observed that as the content of kaolinite-hydromica clay with a montmorillonite admixture from Gaidukovka deposit increases, the diffraction maxima belonging to α-quartz become perceptibly higher, which is accounted for by the high sand content in this clay. However, here the intensity of the hematite peaks first decreases as the content of Lukoml' deposit clay in the mixture decreases, and then it increases sharply. Furthermore, a decrease in the intensity of the main peak of anorthite ($d = 0.3204$ nm) was observed with increase in the content of Lukoml' clay in the mixture, and a slight increase in this peak was observed in mixtures with Gaidukovka deposit clay. At the same time, when this clay prevails in the mixture, the x-ray amorphism of the structure increases to some extent.

It was found that the greatest degree of sintering is achieved in the temperature interval of 950 – 980°C in using a complex flux with a cullet : nepheline-sienite ratio equal to 1 : 1. Here, the sum ($RO + R_2O + Fe_2O_3$) constitutes around 26%, the sum ($RO + R_2O$) is around 18%, and the ratio $RO : R_2O$ is 1.95 – 2.00.

The samples do not exhibit any deformation or a black core. The crock has a uniform red-brown coloring and a homogeneous structure of the fracture.

The electron microscope study of the considered ceramic mixtures fired at a temperature of 1000°C established the following. The sample structure is represented by partially fused quartz grains, a vitreous phase, and an amorphous clay component that forms as a the result of merging of dehydrated kaolinite and hydromica packs. The size of the fused quartz grains distinguishable in the photographs is 11 – 14 μm. The materials have pores, mostly channel-forming pores, of size 6 – 12 μm. As the quantity of flux in the mixture increases, the character of the pores changes: blind pores of size 3 – 7 μm are found. The samples exhibit clusters of fine crystals whose zonal structure is evidence of their heterogeneity. These new short prismatic formations can be classified by morphology either as an anorthite-like phase or as primary mullite appearing in the solid phase from metakaolinite. It should be noted that the crystallization of new formations in the form of crystal clusters (Fig. 1) proceeds directly in the pores of the material. This indicates that the interphase boundaries between the vitreous phase, the amorphous argillaceous component, and the pores are decisive in the crystallization of these ceramic mixtures.

In spite of the variety of known glaze compositions for decoration of majolica products, their choice for each specific case is limited, especially in using single-stage firing, and calls for further research on coordination of the TCLE of glaze coatings and ceramic mixtures and on linking the processes of gas emission from the crock and the character of the formation of the intermediate layer at the site of ceramic – glaze contact and the glaze layer itself.

In analyzing the interrelationship of the thermal effects observed in the glaze coatings, it should be noted that glazes that have a lower softening temperature, greater meltability, and lower viscosity foster better release of gas products from the ceramic crock through the softened glaze layer. The latter, in turn, is able to remove defects of the glaze coating by fusing craters, chips, blisters, etc.

Glazes containing not less than 18 – 20 wt.% B_2O_3 have a positive effect on the qualitative parameters of coatings of single-stage firing. Glazes containing substantial quantities of SiO_2, Al_2O_3, and ZrO_2 apparently have a higher melt viscosity and therefore are more prone to surface defects.

One of the features of the process of firing ceramic mixtures based on polymineral clays is gas emission in the temperature interval of 150 – 350°C, which is caused both by burn-out of organic and humus inclusions contained in the initial raw material and by the processes of iron oxide reduction to the divalent state, as well as by removal of mechanically bound water. Since humus and sulfates are present in clays in insignificant quantities, the gas formation caused by their decomposition is minimal and has no perceptible effect on the glaze coating continuity.

An endothermic effect caused by decomposition of carbonates is observed in all mixtures in a narrowest temperature interval with a maximum at 820 – 860°C. This effect is characterized by high intensity, which creates a conditions for a most significant negative influence upon the quality of the glaze coating. Furthermore, in the last moment of heat treatment, removal of air related to an increase in the pressure inside the pores, especially in blind and open pores, is completed.

Thus, all gas release processes in the mixtures considered are completed at a temperature of about 900°C, and therefore, an isothermal hold at this temperature is required lasting 20 – 30 min.

The features of formation of a transparent glaze coating were evaluated by comparing the number of gas bubbles forming in the glaze layer in one-stage and two-stage firing. This study was carried out on a scanning electron microscope on the area of fresh cleavage of the glaze coating. The main bubble formation parameters were the maximum bubble size and the total number of bubbles of prevalent size per cm^2. The total number of bubbles was calculated using the microscope measuring scale, which at maximum magnification makes it possible to isolate a surface area equal to 0.0002 cm^2 on the investigated object. The number of bubbles of prevalent size was determined on this area. By multiplying the result by 5000, the number of bubbles per cm^2 was obtained. The main defect of the coating was pinholes, which, according to the data in [4], are formed in the case of a critical bubble diameter exceeding 20 μm and constitute up to 5 pinholes in two-stage firing and 3 – 8 pinholes in single-stage firing.

Figures 2 and 3 show the dependence of the adopted parameters of bubble formation in the glaze layer on the time/temperature parameters of firing transparent coatings based on glass of the composition $10Na_2O \cdot 5CaO \cdot 20B_2O_3 \cdot 7.5Al_2O_3 \cdot 57.5SiO_2$. It is observed that in both double-stage and single-stage firing the number of bubbles of all sizes decreases as the heat treatment temperature increases. Furthermore, in two-stage firing, the maximum bubble size first increases, and then in the temperature interval of 950 – 1050°C it decreases. In single-stage firing, this decrease is smooth, with a regular gradual decline in the number of bubbles and in the maximum bubble size.

As regards formation of bubbles in a coating in relation to the duration of the hold at the maximum temperature, as the duration of the hold increases, the number of bubbles decreases in both cases; however, the character of the decrease is similar to the indicated relation.

Thus, an increase in the duration of heat treatment at the optimum firing temperature results in sufficient homogeneity of the coating in both two-stage and single-stage firing, due to the decreased volume of the gas phase, whose presence degrades the coating clarity and leads to formation of the most common glaze defect, namely, pinholes.

A study of the physicochemical properties of transparent glaze coatings indicates that their TCLE is within the limits of $(48 - 56) \times 10^{-7}$ K^{-1}, and the softening onset temperature is 640 – 670°C.

Use of the developed mixture compositions based on the combining of two or more polymineral clays with grog and flux additives makes it possible after drying to obtain a strong low-shrinkage intermediate product capable of resisting soaking when the glaze coating is deposited. In this connection we developed the main technological conditions for

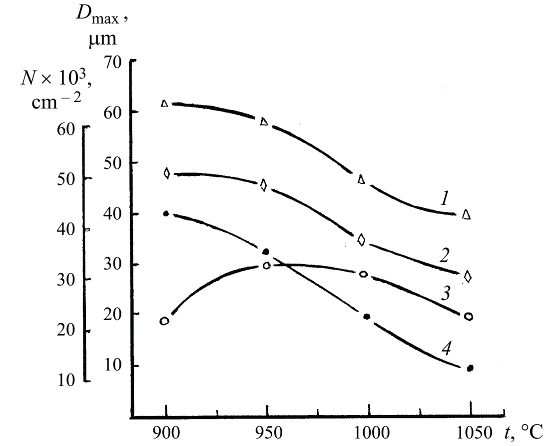

Fig. 2. Effect of the firing temperature on the formation of gas-phase bubbles in the glaze coating structure (a hold of 90 min): *1* and *2*) maximum bubble diameter in two-stage and single-stage firing, respectively; *3* and *4*) number of bubbles of all sizes in two-stage and single-stage firing, respectively.

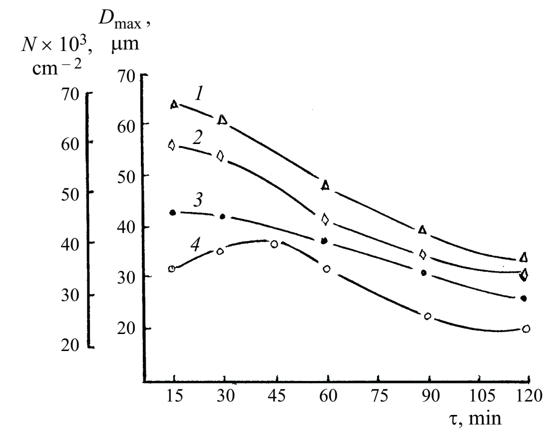

Fig. 3. Effect of the hold duration on the formation of gas-phase bubbles in the glaze coating structure (a firing temperature of 975°C). The same notation as in Fig. 2.

single-stage firing intended to produce majolica products based on the synthesized mixtures and we carried out testing of the developed mixtures and glazes and the single-stage firing technology under industrial conditions at the Belkhudozhkeramika Company.

A trial lot of the following range of products was manufactured: plates, salad bowls, ash-trays, flower pots, etc. Production of the trial lot and acceptance tests of the prototypes demonstrated the suitability of the proposed mixture compositions and the indicated technological conditions for the production of majolica products using the single-stage firing method, implemented in three-channel electric furnaces. The water absorption of the products after the second firing constituted 13 – 16%, the overall shrinkage was 3.0 – 4.5%, and the TCLE was $(6.2 - 7.1) \times 10^{-6}$ K^{-1}, which corresponds to the parameters of products produced by two-stage firing.

Thus, a technology for the production of glazed majolica articles is developed that makes it possible to obtain high-quality products using energy-saving single-stage firing technology.

REFERENCES

1. I. Raht and P. Netik, “Vliv prostredi zwlaste vilhkosti na pevnost keramiky,” *Sklar a keram.*, **34**, 199 – 201 (1984).
2. M. Y. Murray, “The fast firing of ceramic products,” in: *7-th Austral. Ceram. Conf. Proceedings*, Sidney (1976), pp. 27 – 28.
3. I. A. Levitskii and V. A. Biryuk, “Ceramic mixtures for majolica products with improved physicochemical properties,” *Steklo Keram.*, No. 6, 13 – 16 (1997).
4. V. A. Finkel’ and P. I. Berenshtein, “Formation of gas-phase bubbles in the structure of a glaze coating for facing tiles in relation to the firing temperature and the hold duration,” in: *Proc. Inst., NIIStroikeramika* [in Russian], Moscow (1981), pp. 109 – 114.